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Title of paperEvaluation of Ion Intercalation in Conducting Polymers.....

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Redox(polyvinylferrocene) and conducting polymer films(poly-3-methylthiophene and polypyrrole) films have been shown to insert anions and/or cations reversibly during redox cycling in order to maintain charge neutrality. Ionic motions across these polymer films have been attempted with the use of 2 techniques, viz., (1) cyclic voltammetric measurement of effects of electrolyte concentration on shifts in E_{peak} based on the Nernst equation, and (2) Quartz Crystal Microbalance Gravimetry.

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Extended Abstract

Evaluation of Ion Intercalation in Conducting Polymers

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Conducting polymer films, such as poly(vinylferrocene), poly(3-methylthiophene) and polypyrrole, have been studied in different electrolytic solutions by cyclic voltammetry. It was found that the voltammetric peak shifted as the electrolyte concentration was changed. The behavior has been shown to be diagnostic of the ions injected into the polymer films. For a cation-doping polymer, the voltammetric peak shifted in the positive direction as the electrolyte concentration was increased. For an anion-doping polymer, the peak shifted in the negative direction as the electrolyte concentration was increased. The slope of peak shifts was found to be close to a Nernstian slope (59 mV/decade) for all conducting polymers studied, even though poly(3-methylthiophene) and polypyrrole exhibit non-Nernstian behavior.

The diagnostic analysis above mentioned will be compared with the in-situ changes of mass in polymeric films by quartz crystal microbalance (QCM) analysis which we reported earlier(7). Examination of actual mass change measurements vs. that predicted from coulometric charge data can reveal the stoichiometry of charge transfer during these reactions. Polyvinylferrocene and polypyrrole (PPy) have been shown to transfer small anions reversibly during oxidation/reduction processes (ClO_4^- and BF_4^-). For larger polymeric anions, such as polyvinylsulfonate (PVS) and polystyrenesulfonate (PSS), the process in PPy involves cation insertion (during reduction) since the large polymeric anions are effectively trapped within the PPy film. For intermediate sized anions (tosylate), the process appears to be a combination of both anion and cation movement to maintain charge neutrality.

Gold coated AT-cut quartz crystals were obtained from Inficon (East Syracuse, N.Y.). The shear mode (6MHz) crystals had a surface area of 0.33 cm² on which polymer was

electrodeposited (PVF deposited by spin-coating). The frequency shift during oxidation and reduction was measured with a frequency counter (HP5384A) and stored in a personal computer (HP9816). The crystal oscillator circuit included a power source and an oscillator (Inficon XTC).

The experiments were performed in a 4-necked glass cell. Two of the necks were used for gas inlet/outlet and one for the reference electrode (SCE) and the last for the counterelectrode (large area stainless steel). The working electrode was the polymer/gold/quartz attached to the open tube in the bottom of the cell with a silicone sealant.

The electrode potential was controlled by a potentiostat (EG&G PAR 173) and a programmer was used for cyclic voltammetric studies (EG&G PAR 176). The polymer film was treated as rigid since the film thickness was small compared to the thickness of the crystal. The Sauerbrey equation was used to analyze the data:

$$\Delta f = - \frac{2f_0^2}{\sqrt{\rho \Omega \mu}} \frac{\Delta m}{A}$$

PVF and polypyrrole films exhibited ideal reversible behavior in perchlorate electrolyte in acetonitrile. The films inserting only perchlorate, a plot of E_{peak} vs. electrolyte concentration had a slope of -48 (PVF) and -75 (PPy) mV/decade (fig.1). This is close to the predicted value of -59 mV/decade for anion intercalation. For films grown in PF_6^- electrolyte, the observed slope is +80 mV/decade, indicating cation movement to maintain electroneutrality. QCM data also indicated that cations were inserted and released in systems grown with large anions. The authors will discuss the effects of the growth conditions on film characteristics with respect to counterion insertion for films grown with small (ClO_4^-), intermediate (TOS^-), and large polymeric anions (PSS^- and PVS^-).

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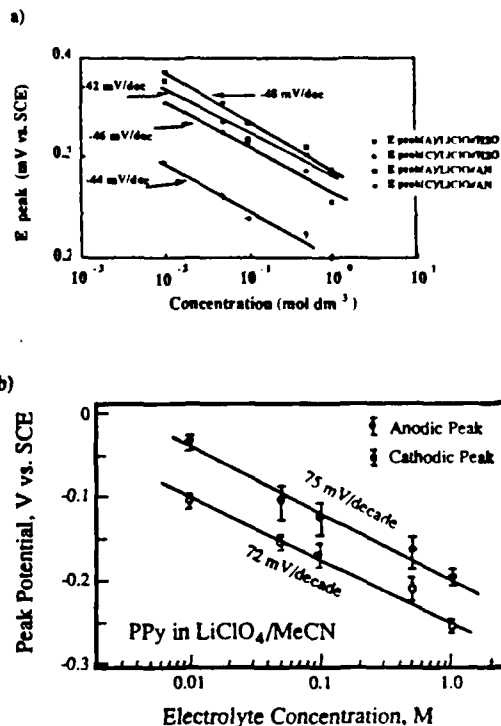


Fig.1 E_{peak} plotted vs. electrolyte concentration for LiClO₄ salt in acetonitrile for a) in PVF b) in PPy.

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